

Dielectric and Ultrasonic Absorption in Some Linear Polyamides

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Synopsis

The dielectric behavior of some linear polyamides has been studied over a frequency range from 10^2 to 10^5 Hz between 20°C and 90°C. Also the change in attenuation of longitudinal ultrasonic waves has been measured as a function of frequency and temperature. Analysis of the results shows α - and β -relaxations. The movement of amide protons involved in intermolecular hydrogen bonds is also noticed.

INTRODUCTION

Dielectric measurements on some polymers were carried out¹ to study the nature of the relaxation processes involved. Polymers containing amide groups are of special interest because of the great strength of the interchain forces and the importance of such structures in proteins and synthetic textiles. For this purpose this work aims to study the relaxation processes of four linear polyamides using ultrasonic and dielectric methods.

EXPERIMENTAL

Four different kinds of polyamides were used, nylon 6, nylon 6.6, nylon 12, and nylon 11. The former three kinds were obtained from Nylonic Engineering Co., Ltd., England, while the latter one was a donation from Professor A. W. Brown, Physics Department, The City University, Northampton Square, London. The physical constants of such materials are illustrated in Table I.

The dielectric constant ϵ' and power factor $\tan \delta$ of the different types of polyamide samples were measured using an NF a Schering bridge-type decimeter in the frequency range between 10^2 Hz and 10^5 Hz. A guard ring capacitor type NFM/5 T was used. Accuracy of measurements in ϵ' was

TABLE I
Physical Constants of the Investigated Polyamides

Material	Nylon 6	Nylon 6.6	Nylon 11	Nylon 12
Grade	31	21	—	51
Specific gravity (gm/cm ³)	1.14	1.14	1.04	1.04
Melting point (°F)	428	491	—	352
Moisture absorption (max) (%)	11	9	0.3	0.8
Coefficient of linear thermal expansion (10 ⁻⁵ /°F)	7.5	6.1	—	6.5

$\pm 1\%$ while for $\tan \delta$ it was $\pm 2\%$. A description of the instrument method used for the measurements and calculations are given in the instruction sheet by Wiss. Techn. Werkstten Weilheim Obb., West Germany (WTW). The samples were in the form of discs 50 mm in diameter and 2.5 mm thick. Measurements were carried out at temperatures between 20°C and 90°C using an ultrathermostat.

The ultrasonic absorption through polyamide samples was measured using a conventional pulse-echo technique.^{2,3} If l is the amplitude of the pulse, d is the distance transversed, l_0 is the pulse amplitude when $d = 0$, and α is the ultrasonic attenuation, the equation relating them can be written in the form

$$l = l_0 e^{-\alpha d}$$

Since the parameter α in polymers is very high and only one or two echos are observed in the oscilloscope, the measurements are taken on a comparative basis. The variation of l^{-1} with temperature is considered to represent the variation of α with temperature. Measurements were carried out at frequency ranging from 2 to 5.7 MHz and temperatures between 25°C and 70°C. The temperature was achieved using an electric furnace.

RESULTS AND DISCUSSION

For nylon 6 and nylon 12, the frequency dependence of ϵ' and ϵ'' at various temperatures are shown in Figures 1 and 2. Values of ϵ' and ϵ'' for nylon 6 obtained here at 10^5 Hz and at 20°C are comparable with those found in

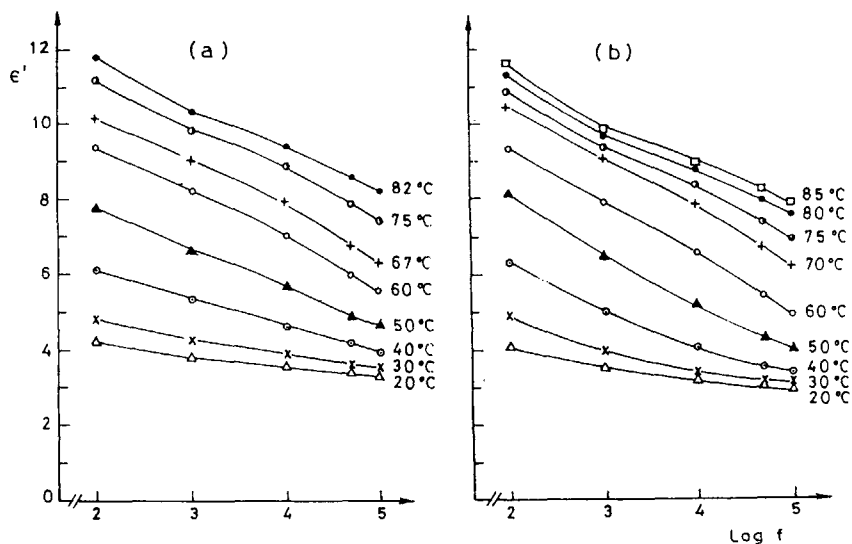


Fig. 1. Frequency dependence of ϵ' at various temperatures for (a) nylon 6 and (b) nylon 12.

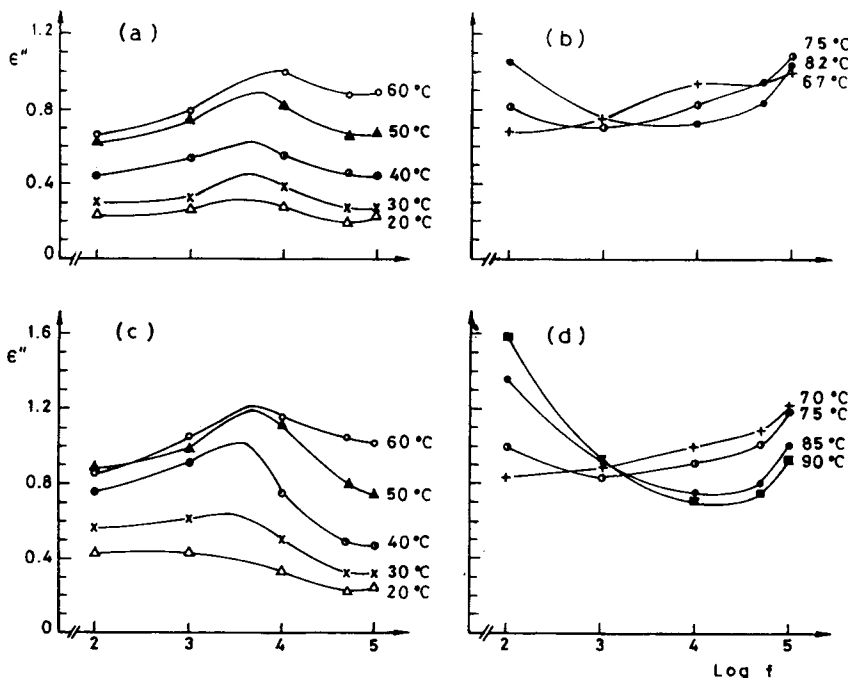


Fig. 2. Frequency dependence of ϵ'' at various temperatures for nylon 6, (a) lower temperature range and (b) higher temperature range, and for nylon 12, (c) lower temperature range and (d) higher temperature range.

literature⁴ ($\epsilon' = 3.90$ and $\epsilon'' = 0.14$). From Figure 2 it is found that at lower temperature, β -absorption is only observed and shifts to higher frequency and becomes sharper and higher with the increase of temperature. This absorption is characteristically due to the side-chain relaxation. At about 70°C the loss region could be resolved into two separate regions. The higher frequency region where the tail of α -absorption appears, but it is possible to identify the position of the peak of β -absorption. This region is attributed to the large scale conformational rearrangements of the main chains.⁵ The second region is the low frequency region where the maximum in the dielectric loss is not reached at the low-frequency limit of the measurements. This region is characterized by extremely high dielectric constant and high dielectric loss. This process which also observed by Baker and Yager⁶ in nylon 610, is undoubtedly due to movements of the proton of the amide group in the hydrogen bond. This can be described as motions of bound charges since the observed dc conduction can only account for a fraction of the observed dielectric losses and cannot account for the enhanced dielectric constants. This process has been found to give rise to marked electret-forming capabilities in these polyamides.⁷

To discuss the data obtained, an analysis was carried out using Cole-Cole plot⁸⁻¹⁰ according to the following equation:

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega\tau_0)^{1-\alpha}]$$

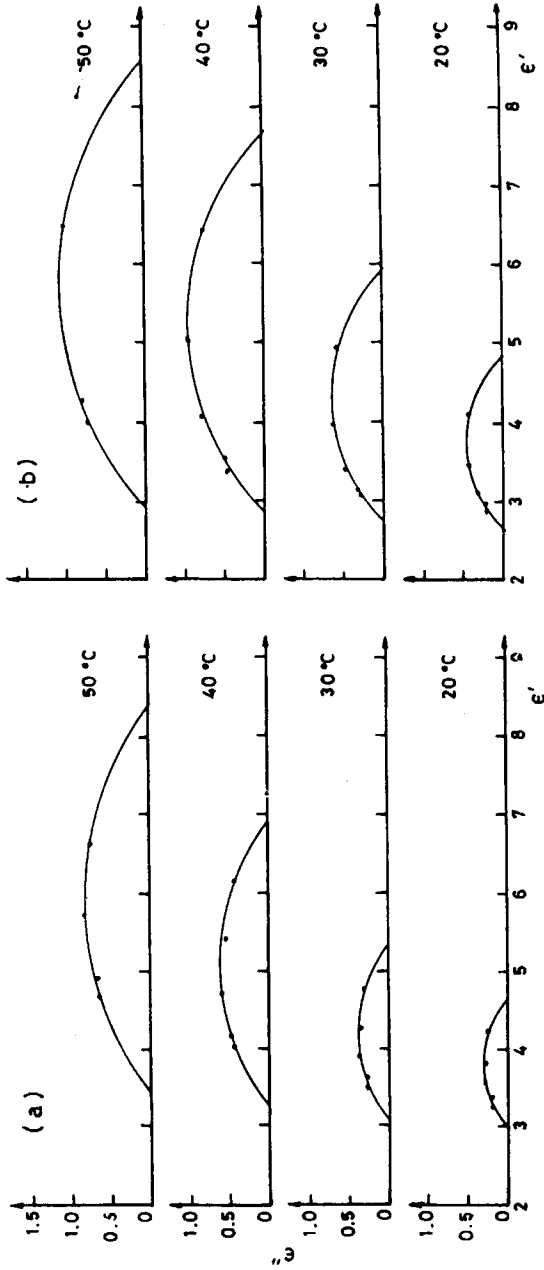


Fig. 3. Cole-Cole plots at various temperatures for β -absorption of (a) nylon 6 and (b) nylon 12.

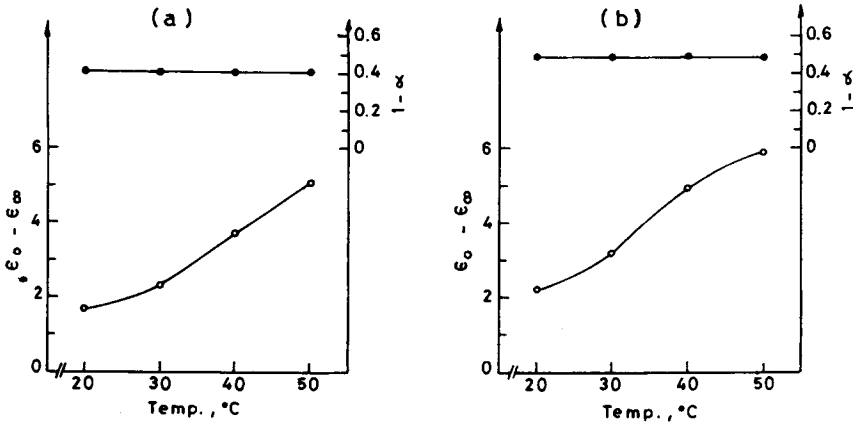


Fig. 4. Temperature dependence of $(\epsilon_0 - \epsilon_\infty)$ and $(1 - \alpha)$ for (a) nylon 6 and (b) nylon 12.

This equation leads to a circular arc in the complex plane with its centre below the real axis by an angle $\alpha\pi/2$ radians. α is an empirical constant and takes the values from 0 to 1 and is regarded as a measure of the distribution of the relaxation time. The generalized relaxation time τ_0 is given by $\tau_0 = 1/2\pi f_m$, where f_m is the frequency corresponding to the loss maximum. ϵ^* is the complex dielectric constant and is defined by the equation $\epsilon^* = \epsilon' - i\epsilon''$. $(\epsilon_0 - \epsilon_\infty)$ corresponds to the length of the chord of the circular arc and represents the magnitude of polarization and is proportional to the concentration of the dipoles which contribute to the dielectric absorption. ϵ_0 is the dielectric constant for the lower frequency (static dielectric constant) and ϵ_∞ is that for the higher frequency (optical dielectric constant).

For both samples and at the different temperatures, ϵ'' is plotted against the corresponding values of ϵ' as shown in Figure 3. The parameter $(\epsilon_0 - \epsilon_\infty)$, which represents the magnitude of the dielectric β -absorption, and also

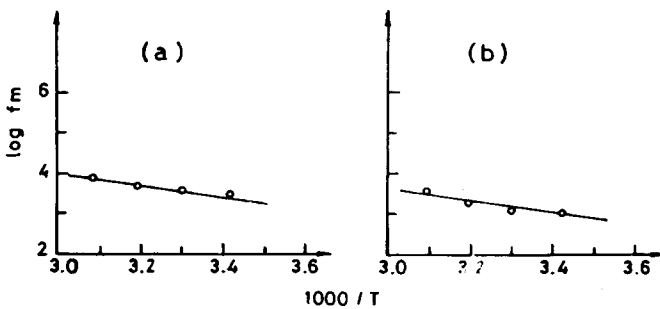


Fig. 5. Relation between $\log f_m$ and $1000/T$ ($^{\circ}\text{K}$) for (a) nylon 6 and (b) nylon 12.

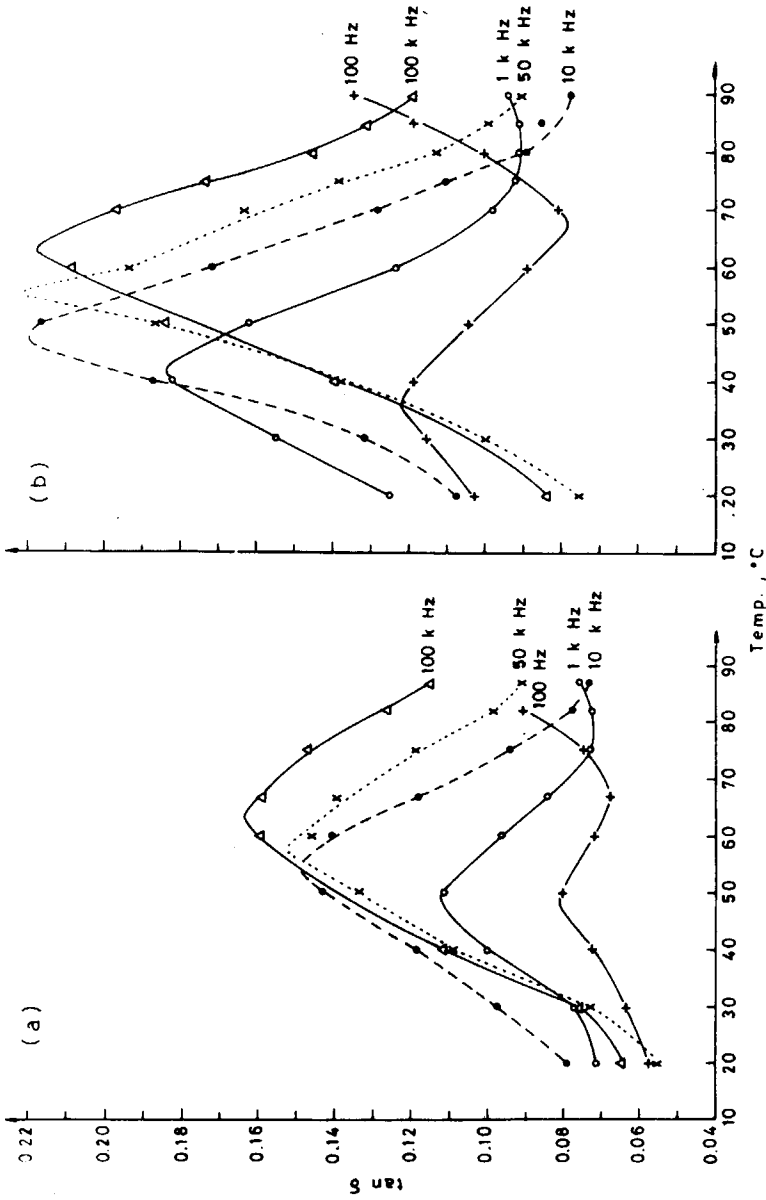


Fig. 6. Temperature dependence of $\tan \delta$ at various frequencies for (a) nylon 6 and (b) nylon 12.

$(1 - \alpha)$, which represents the degree of broadness of the absorption curve, are plotted against the temperature, as shown in Figure 4. $\epsilon_0 - \epsilon_\infty$ is found to increase with temperature while no significant change in $1 - \alpha$ was noticed. This result is similar to that found in the literature⁴ for nylon 6 and poly(vinyl chloride).

In order to calculate the apparent activation energy $\Delta H\beta$ for the dielectric absorption, $\log f_m$ is plotted against the reciprocal of the absolute temperature as shown in Figure 5. From the slope of the straight lines obtained and by using the Arrhenius equation,¹¹ the activation energies were obtained and found to be 7.0 kcal/mol and 6.9 kcal/mol for nylon 6 and nylon 12, respectively. These values are comparable with those found in

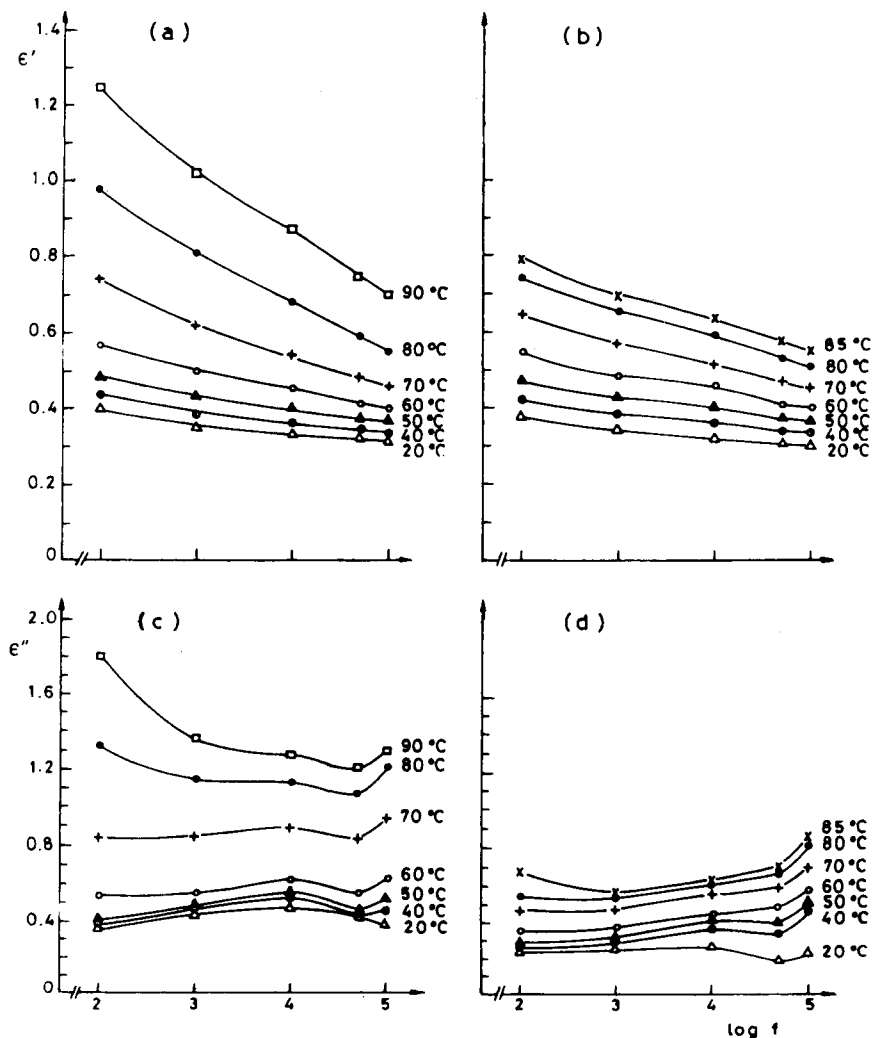


Fig. 7. Frequency dependence of ϵ' and ϵ'' at various temperatures for (a) nylon 11 and (b) nylon 66.

literature^{1,4,7,12} for the β -relaxation process, whether in crystalline or amorphous polymer (7–26 kcal/mol).

The temperature dependence of $\tan \delta$ for both polyamides at the different frequencies is shown graphically in Figure 6. In case of nylon 6, the peaks appear in the region of 47°C (100 Hz) to 63°C (100 kHz) while in case of nylon 12 the peaks appear in the region of 36°C (100 Hz) to 62°C (100 kHz). The rise in $\tan \delta$ noticed at the lower frequencies (100 Hz and 1 kHz) and at temperature above 70°C is most likely due to the motions of the amide group hydrogens as mentioned before.

For nylon 11 and nylon 6.6, the absorption regions which express α - and β -relaxations are not observed in the tested range of frequency and temperature. Anyhow, the data obtained for the dielectric constant and dielectric loss at the different frequencies and temperatures are illustrated graphically in Figure 7. Values of ϵ' and ϵ'' for nylon 6.6 obtained here at 10 kHz and at 20°C are comparable with those found in the literature¹ ($\epsilon' = 3.2$ and $\epsilon'' = 0.1$).

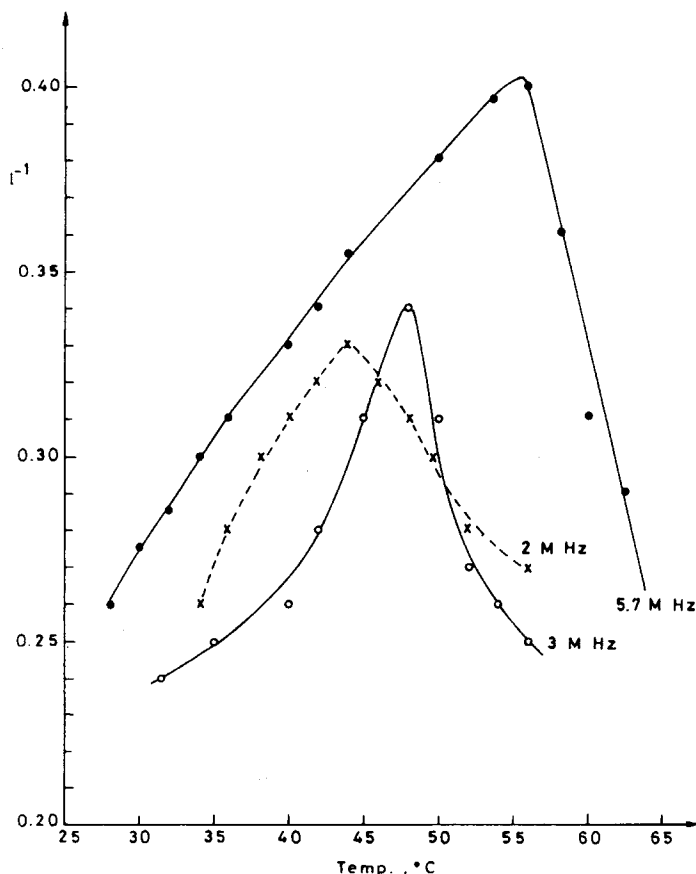


Fig. 8. Relation between l^{-1} and t (°C) at various frequencies for nylon 66 [l (cm) is the height of a particular echo].

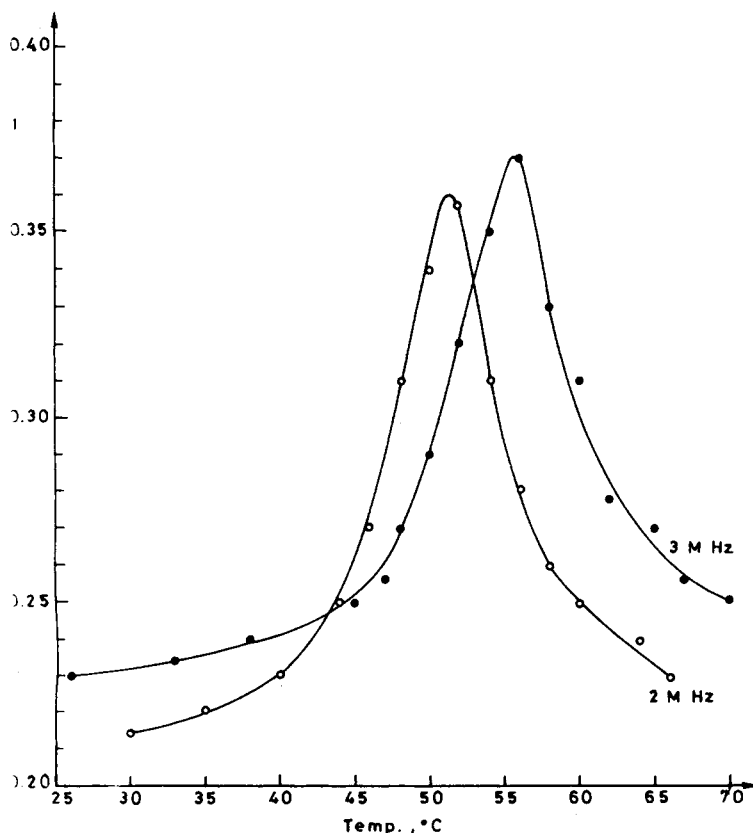


Fig. 9. Relation between l^{-1} and t (°C) at various frequencies for nylon 11.

In order to find out the relaxation of these two polyamides, ultrasonic technique with frequency ranging from 2 MHz to 5.7 MHz was used. The change in attenuation of the longitudinal ultrasonic waves with temperature is shown in Figures 8 and 9. For nylon 6.6, the peaks are observed in the region of 44°C (2 MHz) to 55.5°C (5.7 MHz). These peaks are considered to be the β -relaxation when compared with those found in the literature¹ at a lower range of frequencies [the β -peak was observed in the region of -20°C (65 Hz) to + 10°C (10 kHz)]. When $\log f$ is plotted against $1/T_m$ (the

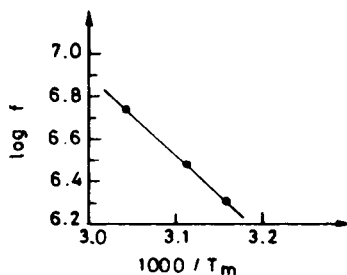


Fig. 10. Relation between $\log f$ and $1000/T_m$ (°K) for nylon 66.

reciprocal of the absolute temperature at which the peak occur), a straight line is obtained, as shown in Figure 10. The apparent activation energy was obtained and found to be 16.9 kcal/mol. This value lies within the range of β -relaxation process of other polymers.

At frequencies 2 MHz and 3 MHz the β -peak for nylon 11 appears at temperatures 51°C and 56°C, respectively. This is a reasonable result when compared with that found in the literature¹ at lower range of frequencies. The β -peak was observed in the region of -55°C (6.8 Hz) to -45°C (125 Hz).

So, it could be concluded that the α -absorption, the β -absorption and the absorption due to the movement of amide protons were observed for nylon 6 and nylon 12, but only the β -absorption for nylon 6.6 and nylon 11.

References

1. N. G. McCrum, R. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solid*, Wiley, New York, 1967, Chap. 12.
2. R. Truell, C. Elbaum, and B. Chick, *Ultrasonic Methods in Solid State Physics*, Academic, New York, 1969.
3. A. W. Aziz, M. Z. El-Sabee, and K. N. Abd-El-Nour, *Acoustica*, **53**, (1983).
4. Y. Ishida, *Kolloid. Z.*, **168**, 29 (1960).
5. R. H. Boyd, *J. Chem. Phys.*, **30**, 1276 (1959).
6. W. O. Baker and W. A. Yager, *J. Am. Chem. Soc.*, **64**, 2171 (1942).
7. A. J. Curtis, *J. Chem. Phys.*, **34**, 1849 (1961).
8. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
9. J. J. Alkonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, 2nd ed., Wiley, New York, 1983, Chap. 8.
10. E. A. Collins, J. Bares, and F. W. Billmeyer, *Experiments in Polymer Science*, Wiley-Interscience, New York, 1983.
11. N. E. Hill et al., *Dielectric Properties and Molecular Behaviour*, Van Nostrand, London, 1969, pp. 316, 424.
12. Y. Ishida, *J. Polym. Sci.*, **7**, 1335 (1969).

Received August 25, 1983

Accepted February 24, 1983